Competing interactions in multiferroics and low-dimensional systems

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Chapter 2

Magnetoelectricity, Multiferroicity, and Electromagnons in Frustrated Magnets

In this Chapter we introduce to magnetoelectric and multiferroic materials. In particular, we discuss simple phenomenological theories, which describe the induction of electric polarization in collinear and non-collinear magnetic states. We consider microscopic mechanisms of magnetoelectric coupling and show that magnetoelectric interactions can give rise to dynamical magnetoelectric effects, such as excitation of a magnon by electric field.

2.1 Linear magnetoelectric effect

The linear magnetoelectric effect - the generation of electric polarization by a magnetic field and *vice versa* - is a fascinating phenomenon predicted by Landau and Lifshitz,[1] and first experimentally observed in 1960 by Astrov and coworkers in chromium oxide.[2; 3] They discovered that a sample of Cr_2O_3 in an external electric field induces a magnetization proportional to the applied field below the antiferromagnetic Néel temperature of 307K. The magnetoelectric effect is described by expanding the free energy in powers of the applied magnetic $\mathbf{H}$ and the electric field $\mathbf{E}$[1]

$$F(\mathbf{E},\mathbf{H}) = F_0 - \frac{\epsilon_{ij}E_iE_j}{8\pi} - \frac{\mu_{ij}H_iH_j}{8\pi} - \alpha_{ij}E_iH_j + \dots \quad (2.1)$$

	Inversion symmetry	Time reversal symmetry
E, **P**	−	+
H ,**M**	+	−
E_iH_j	−	−

Table 2.1 Spatial inversion and time-reversal symmetry properties of electric and magnetic quantities.

Here, E_i (H_i) is the i'th component of **E** (**H**). The first term in the right-hand side of Eq.(2.1) describes the usual dielectric response, were ϵ_{ij} is the permittivity tensor. The second term is the magnetic analogue of the first one, μ_{ij} being the magnetic permeability. The remaining term represents the linear magnetoelectric coupling and α_{ij} is the so-called magnetoelectric tensor. Expressions for the electric and magnetic polarization can be found by differentiating the free energy F with respect to E_i and H_i. We find

$$P_i = \chi^e_{ij} E_j + \alpha_{ij} H_j, \tag{2.2}$$

$$M_i = \chi^m_{ij} H_j + \alpha_{ji} E_j, \tag{2.3}$$

where $\chi^e_{ij} = (\epsilon_{ij} - \delta_{ij})/4\pi$ and $\chi^m_{ij} = (\mu_{ij} - \delta_{ij})/4\pi$ are the dielectric and magnetic susceptibility tensors. Only a limited number of magnetic symmetry classes allow for the linear magnetoelectric coupling α_{ij}. For instance, α_{ij} can only be nonzero for materials that simultaneously break time reversal symmetry T and spatial inversion symmetry I. The most common source of time asymmetry in Mott insulators is spin ordering. The magnetoelectric coupling appears if the spin ordering breaks inversion symmetry.

The components of the magnetoelectric tensor are constrained by thermodynamic stability criteria. Namely, α_{ij} is bounded by the appropriate diagonal elements of the dielectric permittivity and magnetic permeability:

$$\alpha_{ij} \leq \frac{\sqrt{\epsilon_{ii}\mu_{jj}}}{4\pi}. \tag{2.4}$$

This relation was obtained from the requirement that the free energy $F(\mathbf{E}, \mathbf{H})$ must have an absolute maximum at zero electric and magnetic fields, i.e. the sum of the three terms in Eq.(2.1) must be smaller than zero.[1] However, second-order thermodynamic perturbation theory puts a stronger upper bound on α_{ij}. If the diamagnetic contribution to the susceptibility can be neglected, which is usually the case for magnetoelectric materials with localized magnetic moments, the magnetoelectric tensor is bounded by the geometrical mean of

the dielectric and magnetic susceptibilities, i.e.[4]

$$\alpha_{ij} \leq \sqrt{\chi^e_{ii}\chi^m_{jj}}. \tag{2.5}$$

Thus, large electric permittivity and/or a large magnetic permeability are prerequisite for large magnetoelectric effects. In fact this requirement is fulfilled in materials showing a ferroelectric, ferromagnetic or multiferroic phase transition. An example of this kind is the divergence of the magnetoelectric susceptibility in $Co_3B_7O_{13}Br$. This compound undergoes two successive phase transitions.[5] First below 466 K a transition into a ferroelectric phase occurs followed by a transition at $T_c = 16$ K to a magnetoelectric multiferroic state. The component of the magnetoelectric tensor, α_{32}, displays a strong peak around T_c whereas α_{23} does not.[6; 7]

There is an interesting relation between magnetoelectric coupling and magnetic frustration, which results from either competing spin interactions or lattice geometries and leads to a highly degenerate ground state. The outcome of frustration strongly depends on the type of material. For instance, quantum spin-1/2 systems may form a spin liquid,[8] whereas spin ice materials have multiply degenerate disordered ground states.[9] If on the other hand, spins are classical and reasonably isotropic, the competing interactions can give rise to inhomogeneous spin orderings that break inversion symmetry in addition to time reversal symmetry. Furthermore, the upper limit on the magnetoelectric susceptibility can be high, as relatively large magnetic susceptibilities and field-induced phase transitions are commonly found in frustrated magnets. For example the series of rare-earth manganese oxides $R\mathrm{Mn_2O_5}$ are typical multiferroic materials, which show a colossal magnetoelectric effect. It was found that in $\mathrm{HoMn_2O_5}$, an incommensurate commensurate magnetic phase transition was induced by the application of a magnetic field, at which electric polarization is generated.[10] This clearly demonstrates that a magnetic phase transition can drive a ferroelectric phase transition.

So far our discussion of the magnetoelectric effect was limited to the linear response described by to the coupling $\alpha_{ij}E_iH_j$ in the free energy. Often the linear coupling is not allowed by symmetry. However, the free energy expansion Eq.(2.1) will in general contain higher-order contributions like for example the third order terms $\beta_{ijk}E_iH_jH_k$ and $\gamma_{ijk}E_iE_jH_k$. In some materials, the nonlinear terms dominate the magnetoelectric response, an example being the piezoelectric paramagnet $\mathrm{NiSO_4{\cdot}6H_2O}$.[11] Another possible source of magnetoelectric effects is the indirect coupling between electric and magnetic properties via strain.[12] In the pursuit for large magnetoelectric effects, two-phase materials have been designed with strain-coupling between a piezomagnetic and a piezo-

electric materials. In laminate composites of piezoelectric-magnetostrictive materials magnetoelectric voltage coefficients up to 4.68 V/cmOe in Terfenol-D/PZT have been found, an enhancement over single-phase magnetoelectrics of several orders of magnitude.[13]

2.2 Ferroelectricy in spiral magnets

The mechanisms that give rise to cross-coupling between polarization and magnetization are very similar to those that lead to the linear magnetoelectric effect. On a phenomenological level, this coupling is determined solely by symmetry arguments. In particular, spatial inversion reverses the sign of electric polarization P, while magnetization M is left unchanged. Time reversal, in turn, will reverse the sign of M, while the sign of P remains unaffected (see Table 2.1). The fourth-order coupling proportional to P^2M^2 is generally allowed by symmetry. It gives rise to small anomalies in dielectric constants at the magnetic transition, as this fourth-order term is typically rather weak.[14; 15] On the contrary, third-order couplings of the form $PM\partial M$ can have interesting consequences.[16; 17; 18] The third order coupling is linear in P and since it contains a single spatial derivative, it is called Lifshitz invariant. The inhomogeneous coupling allows for two scenarios depending on whether ferroelectric or magnetic order occurs first in the material.

If ferroelectricity occurs first, this term favors an incommensuration of a magnetic ordering. $BiFeO_3$, for example, is an antiferromagnetic ferroelectric with a Néel temperature of ~ 643 K and a ferroelectric Curie temperature of ~ 1103 K.[42] It is a very rare example of a multiferroic with both magnetic and ferroelectric ordering temperatures above room temperature. The primary magnetic order in $BiFeO_3$ is G-type antiferromagnetism, but, in addition, it has been reported that bulk single crystals exhibit a superimposed cycloidal spiral magnetic ordering. [20] Due to the relativistic origin of the Lifshitz invariant $-\lambda PL\partial L$, that couples the Neél vector L and the polarization P, the period of rotation is very long, namely $\lambda = 620$ Å.[21; 22]

If an inhomogeneous magnetic ordering sets in first, then a Lifshitz term in the free energy can induce polarization. Let us consider the free energy that describes the coupling between polarization and nonuniform distributions of magnetization in a cubic environment,[18]

$$F_p = \frac{\mathbf{P}^2}{2\chi^e} - \lambda\mathbf{P}\left[\mathbf{M}(\nabla\cdot\mathbf{M}) - (\mathbf{M}\cdot\nabla)\mathbf{M}\right]. \tag{2.6}$$

The induced polarization can than easily be found by differentiating F with

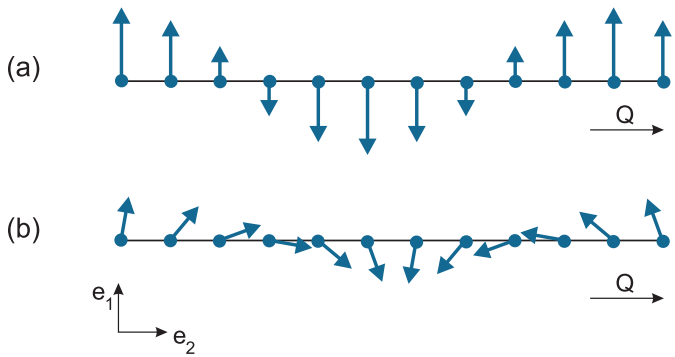

Figure 2.1 Spiral magnetic ordering: (a) sinusoidal spin density wave is symmetric upon spatial inversion and does not induce polarization and (b) a spiral spin density wave which breaks inversion symmetry and induces polarization.

respect to $\mathbf{P}$. One obtains:

$$\mathbf{P} = \lambda\chi^e\left[\mathbf{M}(\nabla\cdot\mathbf{M}) - (\mathbf{M}\cdot\nabla)\mathbf{M}\right]. \tag{2.7}$$

Note that the actual form depends on the symmetry of the lattice. The next obvious question would be what kind of magnetic order can induce polarization. For example, sinusoidal spiral ordering, described by

$$\mathbf{M}_n = M_0\mathbf{e}_1\cos\mathbf{Q}\mathbf{x}_n, \tag{2.8}$$

where $\mathbf{e}_1$ is a unit vector and $\mathbf{Q}$ is the wave vector of the spiral, cannot give rise to polarization. This can be seen by substituting the expression for $\mathbf{M}_n$ into Eq.(2.7) or by noting that $\mathbf{M}_n$ is left invariant under spatial inversion $x_n \to -x_n$. On the contrary, a spiral magnetic state

$$\mathbf{M}_n = M\left[\mathbf{e}_1\cos\mathbf{Q}\mathbf{x}_n + \mathbf{e}_2\sin\mathbf{Q}\mathbf{x}_n\right] \tag{2.9}$$

gives rise to polarization $\mathbf{P} \propto \mathbf{e}_3\times\mathbf{Q}$, where $\mathbf{e}_1$ and $\mathbf{e}_2$ define the spiral plane and $\mathbf{e}_3$ is the spin rotation axis. Thus the induced electric polarization is orthogonal to the propagation vector and lies in the spiral plane. (See Fig. 2.1)

Studying the magnetoelectric and multiferroic properties of frustrated system is interesting, because frustration often leads to spin configurations breaking inversion symmetry. For example, in a one-dimensional Heisenberg chain with antiferromagnetic nearest-neighbor exchange J_1 and ferromagnetic next-nearest-neighbor exchange J_2, the ground state configuration corresponds to

a magnetic spiral state Eq.(2.9) if $J_1 > |J_2|/4$. The wave vector is given by

$$\cos(Q/2) = -\frac{J_2}{4J_1}, \tag{2.10}$$

i.e. it depends on the ratio of the exchange constants.

These simple considerations explain the rich magnetoelectric phases observed in orthorombic rare earth manganites with general formula $R\mathrm{MnO_3}$ (R is a trivalent rare-earth ion) as a function of the ionic radius of R. The ratio between the nearest- and next-nearest-neighbor exchanges in the ab-plane strongly depends on the distortion of the perovskite lattice, which in turn is a function of the radius of R. Due to orbital ordering, the interaction between neighboring spins in the ab-plane is ferromagnetic, whereas nearest-neighbor exchange along the c-axis is antiferromagnetic. As a result the ground state for sufficient large radii (R=La, Nd or Sm) displays A-type antiferromagnetic order, i.e. antiferromagnetically coupled ferromagnetic layers. Yet for $R\mathrm{MnO_3}$ with (R=Tb or Dy) the Mn^{3+} spins in the ab-plane form incommensurate structures. On lowering the temperature a collinear sinusoidal spin-density-wave appears below $T = 40 - 50$ K and on further cooling a transition takes place to a ferroelectric state characterized by incommensurate cycloidal spin ordering.

In $R\mathrm{MnO_3}$ polarization is induced by magnetic order in a material that is otherwise structurally centrosymmetric.[23] In general, systems in which ferroelectricity arises as a secondary effect that is coupled to some other form of ordering, are called "improper ferroelectrics".[24] They are distinct form the "proper" ferroelectrics, in which polarization itself is the primary order parameter of the ferroelectric phase transition. Despite this difference, the dielectric constant ϵ in improper ferroelectrics such as $R\mathrm{MnO_3}$ shows the same kind of anomaly around the transition as in proper ferroelectrics. In addition, the polarization displays "proper" behavior in that it grows steeply as a function of temperature.[25]

The microscopic mechanism involving magnetically induced ionic displacements in spiral ferroelectrics is usually discussed in terms of the antisymmetric Dzyaloshinskii-Moriya (DM) interaction.[26; 27] The DM interaction resembles the form of antisymmetric superexchange interaction that appears in addition to the symmetric Heisenberg exchange ($\mathbf{S}_i \cdot \mathbf{S}_j$) due to relativistic spin-orbit coupling

$$H_{DM} = \sum_{ij} \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j). \tag{2.11}$$

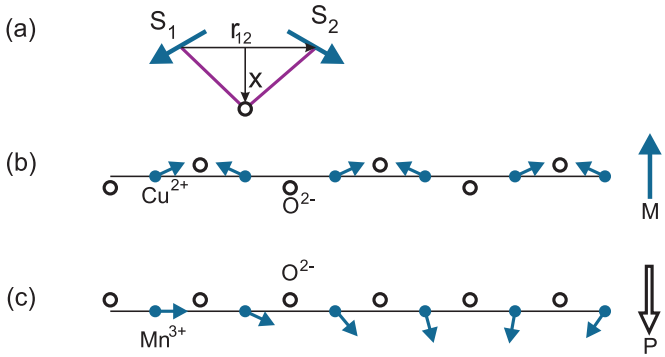

Figure 2.2 (a) Schematic picture of the Dzyaloshinskii-Morija interaction $H_{DM} = \mathbf{D}\cdot(\mathbf{S}_1 \times \mathbf{S}_2)$ with the Dzyaloshinskii-vector $\mathbf{D} \propto \mathbf{x} \times \mathbf{r}_{12}$, which depends on the position of the oxygen ion (open circle) $\mathbf{x}$ and the vector connecting the two transition metal ions $\mathbf{r}_{12}$. (b) Weak ferromagnetism in copper oxide layers of La_2CuO_4. Due to the out-of-plane positions of the oxygen ions the Dzyaloshinskii-vector alternates in the plane and leads to canting of the antiferromagnetic spin. (c) Weak ferroelectricity results from the inverse-Dzyaloshinskii-Moriya mechanism where inhomogeneous magnetic order pushes the oxygen ions out of the plane.

Here λ is the spin-orbit coupling constant, $\mathbf{D}_{ij} \propto \lambda \mathbf{x} \times \mathbf{r}_{ij}$ is the so-called Dzyaloshinskii-vector, where $\mathbf{r}_{ij}$ is the unit vector connecting the magnetic ions i and j, and $\mathbf{x}$ is the distance between the ligand (mostly oxygen) mediating the superexchange and this line. [21; 22] (see Fig. 2.2) To some extend, the further away is the ligand from the axis connecting the magnetic ions, the larger is the DM interaction.

Being proportional to the vector product of spins, the DM interaction favors non-collinear spin ordering. This interaction is known to lead to several phenomena. For example, a common feature of antiferromagnetic oxides, including the parent compound of high-temperature superconductors La_2CuO_4, is the presence of canted spins on the transition metal sublattice.[28] How such a weak ferromagnetism arises from the DM interaction is easily explained with the help of the schematic picture shown in Fig. 2.2(b). Consider a chain of Cu^{2+} spins with nearest-neighbor interactions arising from superexchange via intermediate oxygen ions. The oxygen ions are distorted from the plane formed by the Cu ions, forming a buckled sheet, which results in an alternating Dzyaloshinskii-vector. As a consequence, the low-temperature spin arrangement corresponds to canted antiferromagnet order rather than a pure Néel state.

At the same time, the *inverse* Dzyaloshinskii-Moriya mechanism can give rise to ferroelectricity in spiral magents such as $R\mathrm{MnO_3}$.[27] For the spiral spin structure Eq.(2.9), the vector product $S_i \times S_j$ is equal for each pair of spins. Therefore, the DM interaction pushes the O^{2-} in one direction transverse to the chain of magnetic ions, as a result of which electric polarization is induced (see Fig. 2.2c).

2.3 Ferroelectricity induced by magnetostriction

One might question whether the spin-orbit coupling is the only possible source of magnetically induced ferroelectricity. The answer is obviously no.[29; 30; 31; 32] In fact, collinear spin arrangements in frustrated magnets can induce polarization via a mechanism called exchange striction. In order to see this, we consider a one-dimensional Ising chain with ferromagnetic (FM) nearest-neighbor exchange J_1 and antiferromagnetic (AFM) next-nearest-neighbor exchange J_2, i.e.

$$E = -|J_1| \sum_n \sigma_n \sigma_{n+1} + J_2 \sum_n \sigma_n \sigma_{n+2}, \tag{2.12}$$

where $\sigma_n = \pm 1$ represents the Ising spin at site n. For $J_2 > |J_1|/2$ the ground state configuration corresponds to a two up two down state.[33] Following reference [34], we assume that two species of magnetic ions, for instance Mn^{3+} and Mn^{4+}, alternate along the chain. In this case the collinear $\uparrow\uparrow\downarrow\downarrow$ spin ordering breaks inversion symmetry and sets the stage for magnetically induced ferroelectricity. Magnetostriction, which is always present, will pull parallel spins to each other and stretch bonds between antiparallel spins, leaving behind net polarization as shown in Fig. 2.3.

In order to describe the charge ordered Ising chain with competing FM and AFM interactions in phenomenological Landau theory, we need two order parameters, namely

$$\begin{aligned} L_1 &= \sigma_1 + \sigma_2 - \sigma_3 - \sigma_4 \\ L_2 &= \sigma_1 - \sigma_2 - \sigma_3 + \sigma_4 \end{aligned}$$

which represent two distinct types of $\uparrow\uparrow\downarrow\downarrow$ order. In terms of L_1 and L_2 the coupling inducing polarization reads $\lambda P(L_1^2 - L_2^2)$.[24] It is of second order in order parameters and does not contain gradients.

The coexistence of site-centred charge ordering and spin ordering of the upupdowndown type has been observed in $R\mathrm{NiO_3}$.[35] Furthermore, this example is closely related to origin of ferroelectricity in orthorombic $R\mathrm{Mn_2O_5}$

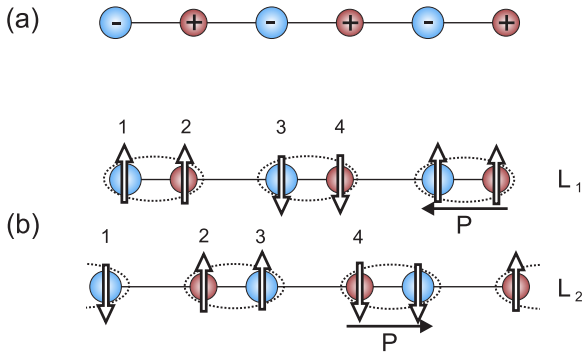

Figure 2.3 Ferroelectricity in a charged ordered chain. (a) A charged ordered chain consisting with red (blue) spheres representing more (less) electric charge. (b) The spin ordering of the type up-up-down-down breaks spatial inversion in the charge ordered chain and induces polarization via magnetostriction. L_1 and L_2 denote the two degenerate ground states with respectively $\uparrow\downarrow\downarrow$ and $\uparrow\downarrow\downarrow\uparrow$.

(R = rare-earth). In this family of multiferroics the strongly interacting Mn^{3+} and Mn^{4+} spins form a five-fold loop of antiferromagnetic bonds which leads to frustration.[29] As a consequence RMn_2O_5 exhibit complex magnetic orderings and rich phase diagrams to be further discussed in Chapter 3 of this thesis.

In microscopic models the spin-lattice coupling results from exchange interactions between spins, such as the isotropic Heisenberg exchange and the Dzyaloshinskii-Moriya interaction, being dependent on the relative positions of the ions. Since Heisenberg exchange is the strongest interaction between spins in transition metal oxides, this type of exchange is likely to be the strongest source of magnetoelectric coupling.

Next we examine the spin-lattice coupling proportional to the scalar product of spins $\mathbf{S}_1 \cdot \mathbf{S}_2$ arising from superexchange. Consider two magnetic ions coupled through an intermediate oxygen ion. The exchange constant coupling between the spins strongly depends on the bond angle ϕ (see Fig. 2.4a). According to the Anderson-Kanamori-Goodenough rules, the exchange is antiferromagnetic ($J > 0$) for $\phi = 180°$ and ferromagnetic ($J < 0$) for $\phi = 90°$.[36] If u is the distance of the oxygen ion to the line connecting the magnetic ions, then to first order in u the exchange interaction has the form

$$H_{ex} = [J(0) + J'u]\mathbf{S}_1 \cdot \mathbf{S}_2 \tag{2.13}$$

where typically $J(0)$ is positive and $J' = dJ/du$ depends on the the angle ϕ.

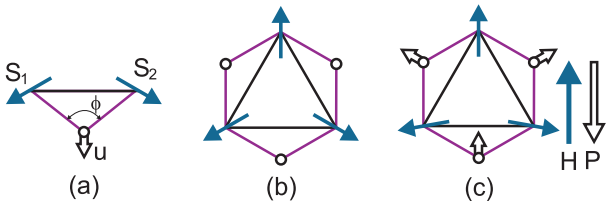

Figure 2.4 (a) A three-atom unit consisting of two magnetic transition metal ions (blue arrows) connected by oxygen (open circle) that mediates superexchange. According to the Anderson-Kanamori-Goodenough rules, the exchange is antiferromagnetic ($J > 0$) for $\phi = 180°$ and ferromagnetic ($J < 0$) for $\phi = 90°$. (b) A spin triangle with antiferromagnetic exchange has 120° ordering in the ground state. (c) Magnetoelectric response of the spin triangle: due to an in-plane magnetic field the spins cant towards the field thereby inducing shifts of the negatively charged oxygen ligands giving rise to electric polarization (big open arrow).

To this we add the harmonic lattice energy $H_{lat} = (K/2)u^2$. In an electric field the positively charged magnetic ions will shift in the direction of the field whereas, ligands tend to displace in the opposite direction, thereby changing the exchange integral and ultimately the spin configuration. Conversely, a magnetic field will change the spin configuration and subsequently lead to a relative shift of the ions, affecting the dipole moment.[37]

To see this concept at work, we analyze a spin triangle with antiferromagnetic exchange mediated by intermediate oxygen ions. If we assume that the spins are confined to the triangle plane the spin energy is minimized if the spins are at 120° from each other. (See Fig. 2.4b) It is easy to show that an in-plane magnetic field applied to this spin arrangement induces via the spin-lattice coupling an electric dipole in the direction of the magnetic field:

$$P_i = \frac{6e\mu_B S J'}{J(0)K} H_i \tag{2.14}$$

which is valid for $i = x, y$. Here e is the unit charge, μ_B the Bohr magneton and K is the harmonic force constant acting when an oxygen ion moves from its equilibrium position.

2.4 Electromagnons

Having discussed the static and ground state properties of magnetoelectric coupled systems, the obvious next step is to study their dynamic features. In this context, we recall that in proper ferroelectrics, anomalies in dielectric

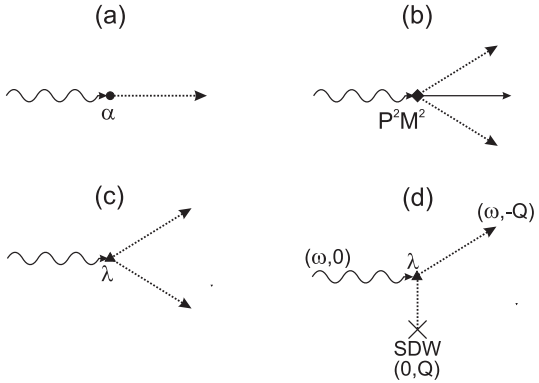

Figure 2.5 Photo-excitation of magnons. Here curly lines represent magnons, dashed lines photons and solid lines denote phonons. (a) Single magnon excitation through the magnetic dipole coupling of the light. (b) Photoexcitation of a three particle continuum consisting of two magnons and a phonon via the fourth order coupling. (c) A single photon excites two magnons via the third order magnetoelectric coupling proportional to λ and (d) photoexcitation of a single magnon with wave vector $-Q$ and frequency ω of the light, where Q is the wave vector of the magnetic structure

constant and other response functions are closely related to the softening of a polar phonon mode.[38; 39; 40] One might wonder what kind of soft mode exists in improper multiferroics, where magnetism induces polarization. This question is closely related to another fundamental question: "What are the lowest-energy excitations in these multiferroics?"

The strong coupling between the magnetic and lattice degrees of freedom can give rise to complex excitations, called electromagnons. They are mixed magnon-phonon excitations, which have the appearance of a magnon that can be excited by electromagnetic radiation. Photoexcitation of magnons is in principle also possible in ordinary magnets. For example, the fourth order spin lattice coupling P^2M^2 can give rise to a process that converts a single photon into two magnons and a phonon.[41] Furthermore, magnons can be excited by the magnetic field of light. This antiferromagnetic resonance is however rather weak as it is proportional to the fine structure constant squared. On the other hand, in multiferroics the third order spin lattice coupling ($PM\partial M$ or PM^2), can lead to a single magnon-excitation by means of an oscillating electric field.[43] To see this, one M should be replaced by the static magnetization, present in the ordered spin state, with the wave vector Q and zero frequency. The other M should be substituted by the magnon with wave vector $-Q$ and frequency ω of the photon (see Fig. 2.5). Thus a photon of frequency ω can

excite a magnon with the same frequency and wave vector Q of the spiral.

Recently electromagnons have been observed in non-collinear spin phases of two groups of multiferroic orthorombic manganites, $R\mathrm{MnO_3}$ (R = Gd, Tb, Dy, $\mathrm{Eu_{1-x}Y_x}$) and $R\mathrm{Mn_2O_5}$ (R = Y, Tb). [44; 45; 46; 47] Electromagnons in both these families have very common feature: they are only active in one polarization direction. For $R\mathrm{MnO_3}$ the electric field component of the light is parallel to the crystallographic a-axis, whereas for $R\mathrm{Mn_2O_5}$ electromagnons are only active for polarization directed along the b-axis. As mentioned above, the fundamental issue is whether the microscopic origin of electromagnons in the different classes of compounds is of the Dzyaloshinkii-Moriya or of Heisenberg type.

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